Domain-wall orientations in ferroelastics

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The orientations of domain walls in ferroelastic materials are theoretically investigated. The procedure followed is based on the same criterion of spontaneous strain compatibility defined by Fousek and Janovec for ferroelectric crystals. Two given domains in a ferroelastic are found to be separated by a planar wall whose orientation belongs to a set of two mutually perpendicular orientations. Domain walls are not always crystallographically prominent planes of fixed indices (W planes) and can instead be determined by the relative magnitude of the components of the second-rank tensor representing the spontaneous strain (W' walls). In the latter case the orientation is expected to be temperature dependent. It is also shown that symmetry considerations are sufficient to find all W planes. According to the considered ferroelastic species the pair of permissible walls between two domains can be two W planes, or a W plane and a W' plane, or two W' planes. The situation where no permissible walls are expected is of particular interest and is examined in known crystals. The predicted orientations of walls are given for the 94 species of full ferroelastics. Available experimental data of the literature are all consistent with our results.

I. INTRODUCTION

A crystal is a ferroelastic if it has several "orientation states" (OS), identical or enantiomorphous in their crystal structure but different with respect to their spontaneous strain.[1] Every OS can be considered as a tiny distortion, issued from slight displacements of the atoms, of a certain ideal structure called its "prototype." The spontaneous strain characterizes the distortion of each OS relative to the prototype structure. This kind of strain occurs at null stress in the same way as the spontaneous polarization occurs in a ferroelectric material in the absence of any electric field. A ferroelastic crystal generally undergoes a phase transition at a temperature T_c into a phase possessing the same structure as the prototype. On the other hand, an appropriate mechanical stress can reversibly transform the crystal from one to another of the OS. This is usually a way of checking the ferroelasticity of a new compound. Since they are energetically equivalent, different orientation states can coexist in the same crystal, which thus becomes twinned. The aim of this work is to find the directions of domain walls which are the boundaries between two OS in a ferroelastic crystal.

Boundaries will be orientated in order to maintain a strain compatibility between two adjacent domains. More precisely, we make the basic assumption that such boundaries (domain walls) must contain all directions for which the change in length of any infinitesimal vector of the prototype, owing to the spontaneous strain, take the same value in the two adjacent domains. In a previous work, Fousek and Janovec[2] have applied the same criterion to the search for the orientations of permissible walls in ferroelectric materials. In the latter class of materials, the strain was then considered as arising from the occurrence of the spontaneous polarization through piezoelectric and electrostrictive effects and was not a primary effect. The validity of the method used in Ref. 2 is thus questionable. Moreover, the relevant piezoelectric and electrostrictive components are often unknown and the actual solving of the problem is not possible. Finally if the relation between spontaneous strain and spontaneous polarization given in Ref. 2 is true for proper ferroelectrics like KH_2PO_4 (KDP), it is no more true for improper ferroelectrics[3] like $Gd_2(MoO_4)_3$.

In Sec. II, starting from the basic assumption, the determination method of the orientation of domain walls in ferroelastics is given. The complete resolution of the problem follows from symmetry properties of spontaneous strain tensors. It is also valid for ferroelastics, which are at the same time ferroelectrics.

The orientations of domain walls are expressed for all ferroelastic species; then follows a list of ferroelastic materials issued from an extensive search in the literature. Domain structures have been already observed in most of them and confirm our predictions (Sec. III).

Section IV is devoted to the situation where between two domains no permissible walls are expected. This does not exclude the possibility for the two considered domains to be adjacent, but leads to stressed boundaries between them. In Sec. V some properties of permissible domain walls are analyzed.

II. DETERMINATION METHOD OF DOMAIN-WALL ORIENTATIONS

The spontaneous strain tensor characterizing an OS is a symmetrical tensor of rank 2 which possesses all the symmetries of the point group of the crystal under consideration. Moreover, the inversion is a symmetry element, as for every even rank tensor. The spontaneous strain tensor has other symmetries resulting from its definition, which reduce the number of independent components. For instance, the trace of this tensor is equal to zero (this means that the strain occurs without change in the volume of the prototype). Aizu has written[4] the form of the spontaneous strain tensor for all OS and for all ferroelastic species. The components of this tensor are referred each time to an orthogonal system x, y, and z of the prototype phase in keeping with the conventional rules.[5]

As pointed out in Ref. 6 the form of the spontaneous strain tensor depends only on the point groups L_p and L_f, these two classes being the holohedry or the hemihedry[7] of the crystalline system to which the prototypic and the ferroelastic phases, respectively, belong. L_p and L_f are obtained by adding the inversion to the point groups of these two phases. L_f is a subgroup of L_p in the same manner as the point group of the ferroelastic phase is a subgroup of the prototype point group. I will therefore limit my investigations to the following 11 Laue crystal classes: $m3m$ (labeled cubic 1), $m3$ (cubic 2), $6/mmm$ (hexagonal 1), $6/m$ (hexagonal 2), $4/mmm$ (tetragonal 1), $4/m$ (tetragonal 2), $\bar{3}m$ (trigonal 1), $\bar{3}$ (trigonal 2), mmm (orthorhombic), $2/m$ (monoclinic), and $\bar{1}$ (triclinic).

Let S be an arbitrary OS in a ferroelastic. All operations of L_f keep its spontaneous strain tensor unchanged, though symmetry operations of L_p which do not belong to L_f change this tensor to a tensor characterizing a different orientation state S'. Generally between two orientation states S and S', there are several such operations (labeled F).

In the orthogonal coordinate system x, y, z of the prototypic phase, let S_{ij} be the components of the spontaneous strain tensor associated with S, and a_{ij} the representative matrix of F^{-1}. The components S'_{ij} in the orientation state S' in the same referential are given[5] by

$$S'_{ij} = a_{ik} a_{jl} S_{kl} \ . \tag{1}$$

When an infinitesimal vector $d\vec{x}$ of the prototype parallel to the unit vector $\vec{s}$, is subjected to a small strain of components S_{ij} (usually S_{ij} are of the order of 10^{-3} or less in ferroelastics), the change in length[8] is then

$$S_{ij} s_i s_j |d\vec{x}| \ . \tag{2}$$

The spontaneous strain being homogeneous, the change in length of a vector of components x_i and of length l is deduced by integration of Eq. (2) and is given by

$$S_{ij} x_i x_j / l \ . \tag{2'}$$

Now, if we take the origin 0 of our coordinate system on the boundary between two domains S and S', according to our basic assumption, the equation of this surface is

$$(S_{ij} - S'_{ij}) x_i x_j = 0 \ . \tag{3}$$

Equation (3) is representative of a cone of apex 0. Owing to the fact that the surface must be independent of the origin chosen on it, the cone which possesses a singular point must be rejected as a physically unacceptable solution of the problem unless it degenerates into a plane. This condition is expressed by

$$\det |S_{ij} - S'_{ij}| = 0 \ . \tag{4}$$

When Eq. (4) is satisfied two planar solutions are permissible. S_{ij} and S'_{ij} being traceless matrices, the two planes are always perpendicular. The case when Eq. (4) is not satisfied will be treated in detail in Sec. IV.

Equation (3) can sometimes be solved by symmetry considerations. Suppose among F operations between S and S', there is a mirror plane W. It is clear that for every vector taken on the surface of W, the change in length due to spontaneous strain is the same in S and S'. Consequently W is a permissible wall between S and S'. Thus, every mirror plane W of L_p which is not present in L_f is a permissible domain wall in a twinned ferroelastic. These W are crystallographically prominent planes of fixed indices. More precisely their orientations are defined by the equation

$$ax + by + cz = 0, \tag{5}$$

where a and b can take only one of the values 0, ± 1, and $\pm\sqrt{3}$, and c is equal to 0 or ± 1. Equation (5) represents the set of all possible mirror planes of the 32 crystallographic point groups.

It can be easily proved that a symmetrical tensor of rank 2 is transformed in the same manner either by a symmetry with respect to a diad axis or by a mirror plane perpendicular to that diad axis. Consequently, if between the spontaneous strains of S and S' a diad axis is an F operation, the plane which is perpendicular to this axis is a mirror between them, and vice versa. In this case, the mirror is one of the permissible walls and the other wall contains the diad axis. The precise orientation of this latter domain wall depends on the relative values of the components of the spontaneous strain tensor at the crystal temperature.

In the most general case, symmetry considerations do not give the orientations of all permissible domain walls. To obtain the complete set of domain walls, it is actually necessary to proceed to a systematic resolution of Eq. (3), i.e., to use the form of the spontaneous strain tensor in the different OS.

Let us apply the procedure defined in this section to the examples of $Gd_2(MoO_4)_3$ and $Pb_3(PO_4)_2$. Twinned $Gd_2(MoO_4)_3$ crystals[9] have two OS differing in spontaneous strain as well as in spontaneous polarization. The prototype point group is $\bar{4}2m$ and the ferroelastic point group is $mm2$. The Aizu species are then $\bar{4}2mFmm2$ as in KDP and Tanane, etc., ... The orthorhombic axes X and Y are turned by 45° with respect to the x, y axis of the tetragonal phase; the orthorhombic axis Z is parallel to the tetragonal axis z. From one OS to the other, the X and Y axes are exchanged. The spontaneous strain is equivalent to a contraction along one of the orthorhombic axes and an expansion along the other, both equal to $(b-a)/(b+a)$, where a and b are the lengths of the axes. L_p and L_f are, respectively, $4/mmm$ and mmm. Among F operations there are the mirrors constituted by the coordinate planes $x=0$ and $y=0$. These planes are the only permissible domain walls. In this example the orientations of domain walls have been derived only from symmetry considerations. Besides, in the case of $Gd_2(MoO_4)_3$, domain walls are planes for which the change in length due to spontaneous deformation is null in every direction. This situation occurs in a ferroelastic each time there are only two different OS (see the demonstration in the Appendix).

Let us now consider the case of $Pb_3(PO_4)_2$, which is a pure ferroelastic[10] belonging to the $\bar{3}mF2/m$ species. The point groups of the ferroelastic and the prototypic phase are, respectively, identical with L_f and L_p. Among F operations from any OS to any other, there are the three mirror planes $y=0$, $y=\sqrt{3}x$, and $y=-\sqrt{3}x$. Let us consider one of the OS, for example, S_1, which has the monoclinic axis parallel to y. The form of the spontaneous strain tensor of S_1 is[4]

$$\begin{pmatrix} -a & 0 & c \\ & a & 0 \\ & & 0 \end{pmatrix} .$$

If x_1, x_2, x_3, and β are the monoclinic lattice parameters, the relation between the spontaneous strain components a and c and these crystalline parameters is given by[11]

$$a=(x_2-x_3/\sqrt{3})/2x_2 \ , \tag{6}$$

$$c=(x_3+3x_1\cos\beta)/6x_1\sin\beta \ . \tag{7}$$

If we label S_2 and S_3 the OS deduced from S_1 by a ±120° rotation around z axis, the spontaneous strain components of these OS written in the orthogonal coordinate system of the trigonal phase are, respectively,

$$\begin{pmatrix} \frac{1}{2}a & \frac{1}{2}\sqrt{3}a & -\frac{1}{2}c \\ & -\frac{1}{2}a & \frac{1}{2}\sqrt{3}c \\ & & 0 \end{pmatrix} \text{ and } \begin{pmatrix} \frac{1}{2}a & -\frac{1}{2}\sqrt{3}a & -\frac{1}{2}c \\ & -\frac{1}{2}a & -\frac{1}{2}\sqrt{3}c \\ & & 0 \end{pmatrix} .$$

When formulating Eq. (3), for instance, between the OS S_2 and S_3, one obtains

$$xya+yzc=0,$$

which gives the orientations of domain walls between S_2 and S_3

$$y=0 \quad \text{and} \quad xa+zc=0 \ . \tag{8}$$

The other domain walls are deduced from these planes by a ±120° rotation around the z axis and separate the OS S_1 and S_3, or S_1 and S_2. Their orientation is indicated in Table IV, part 11. Let us consider relation (8): the first plane is a prominent plane (W wall). The second plane contains the y axis and is a W' plane. Note that the y axis is precisely a symmetry element of $\bar{3}m$ which does not belong to the point group of S_2 and S_3 but is an F element between them. The z axis remains unaltered by the spontaneous strain; the angle that the W' planes make with this axis is given by

$$\tan\theta=-c/a \ . \tag{9}$$

The values of a and c at room temperature are[11]

$$a=21.8\times10^{-3} \quad \text{and} \quad c=6.6\times10^{-3} \ .$$

By replacing a and c in Eq. (9), one obtains $|\theta| = 17°$, in good agreement with the experimental value.[10] Hence, the theory is able to predict the orientation of W' domain walls as well as W domain walls.

III. DOMAIN-WALL ORIENTATIONS IN THE 94 SPECIES OF FULL FERROELASTICS

We have determined the equations of the directions of planes of permissible domain walls be-

TABLE I. Domain-wall orientation in ferroelastics, tetragonal system.

Cubic 1 → Tetragonal 1 (3 ; 6)	
$432F422$, $\bar{4}3mF\bar{4}2m$, $\underline{m3mF4/mmm}$	
$\begin{pmatrix} -2b & 0 & 0 \\ & b & 0 \\ & & b \end{pmatrix}$	tetragonal axis parallel to x
x = y	x = - y
y = z	y = - z
z = x	z = - x

TABLE II. Domain-wall orientations in ferroelastics, orthorhombic system.

1. Cubic 1 → Orthorhombic (S) (6 ; 21)
432F222 , $\bar{4}3mFmm2$, $\underline{m3mFmmm}$

$$\begin{pmatrix} -2b & 0 & 0 \\ & b & d \\ & & b \end{pmatrix}$$ orthorhombic axis parallel to x

x = 0	y = 0
y = 0	z = 0
z = 0	x = 0
x = y	3b(x+y) + 2dz = 0
x = y	3b(x+y) - 2dz = 0
x = -y	3b(y-x) + 2dz = 0
x = -y	3b(y-x) - 2dz = 0
y = z	3b(y+z) + 2dx = 0
y = z	3b(y+z) - 2dx = 0
y = -z	3b(z-y) + 2dx = 0
y = -z	3b(z-y) - 2dx = 0
z = x	3b(z+x) + 2dy = 0
z = x	3b(z+x) - 2dy = 0
z = -x	3b(z-x) + 2dy = 0
z = -x	3b(z-x) - 2dy = 0

2. * Cubic 1 → Orthorhombic (P) (6 ; 6)
432F222 , $\bar{4}3mF222$, $\underline{m3mFmmm}$

$$\begin{pmatrix} a & 0 & 0 \\ & b & 0 \\ & & c \end{pmatrix}$$ a + b + c = 0

x = y	x = -y	x3
y = z	y = -z	x3
z = x	z = -x	x3

3. * Cubic 2 → Orthorhombic (3 ; 0)
23F222 , $\underline{m3Fmmm}$

$$\begin{pmatrix} a & 0 & 0 \\ & b & 0 \\ & & c \end{pmatrix}$$ a + b + c = 0

No permissible domain walls

4. Tetragonal 1 → Orthorhombic (S) (2 ; 2)
422F222 , 4mmFmm2 , $\bar{4}2mFmm2$, $\underline{4/mmmFmmm}$

$$\begin{pmatrix} 0 & a & 0 \\ & 0 & 0 \\ & & 0 \end{pmatrix}$$ orthorhombic axis making 45° with x

x = 0 y = 0

5. Tetragonal 1 → Orthorhombic (P) (2 ; 2)
422F222 , 4mmFmm2 , $\bar{4}2mF222$, $\underline{4/mmmFmmm}$

$$\begin{pmatrix} -a & 0 & 0 \\ & a & 0 \\ & & 0 \end{pmatrix}$$

x = + y x = - y

6. Hexagonal 1 → Orthorhombic (3 ; 6)
622F222 , 6mmFmm2 , $\bar{6}m2Fmm2$, $\underline{6/mmmFmmm}$

$$\begin{pmatrix} -a & 0 & 0 \\ & a & 0 \\ & & 0 \end{pmatrix}$$ orthorhombic axis parallel to x

x = 0	y = 0
x = $\sqrt{3}$ y	y = $-\sqrt{3}$ x
x = $-\sqrt{3}$ y	y = $\sqrt{3}$ x

tween all possible OS for all symmetries compatible with ferroelasticity. In a ferroelastic which has n different OS, there are at most $n(n-1)/2$ couples of mutually perpendicular domain-wall orientations.

Aizu has found 94 species of full ferroelastics; 42 of them are simultaneously full ferroelectrics. The number of OS in a full ferroelastic (full ferroelectric) is equal to the order of the prototypic point group divided by the order of the ferroelastic (ferroelectric) point group.[12]

We report in Tables I, II, III, IV, and V, the orientations of the domain walls of the 94 species. Each table is relative to the crystallographic system to which the ferroelastic phase belongs. Species which possess the same form of spontaneous strain tensors are arranged in the same paragraph. The crystalline systems between which the ferroelastic transition occurs are stated in the first line of each paragraph. On the same line, the number

TABLE III. Domain-wall orientations in ferroelastics, trigonal system.

Cubic → Trigonal	(4 ; 9)	
$23F3$, $m\bar{3}F\bar{3}$, $432F32$, $\bar{4}3mF3m$, $\underline{m3mF\bar{3}m}$		
$\begin{pmatrix} 0 & d & d \\ & 0 & d \\ & & 0 \end{pmatrix}$	trigonal axis parallel to [111]	
$x = 0$	$y = z$	
$x = 0$	$y = -z$	
$y = 0$	$z = x$	
$y = 0$	$z = -x$	
$z = 0$	$x = y$	
$z = 0$	$x = -y$	

of ferroelastic OS, followed by the number of crystallographically different permissible walls, are specified in parentheses. The ferroelastic species concerned are listed. Those associated to transitions between L_p and L_f are underlined. Then, the strain tensor of one of the OS is written in matrix form and in the same notation as in Ref. 4 (this OS is specified to the right of the matrix). Finally the orientations of the permissible walls are given in the rectangular coordinate system of the prototypic phase. On the same line are indicated the orientations of the two permissible mutually perpendicular planes corresponding to the same set of OS without specification of the OS concerned, for simplicity. An asterisk indicates the paragraphs where, between certain OS, no permissible walls are expected. In order to avoid too long enumeration, a condensed notation is sometimes used for triclinic ferroelastics: the symbols ϵ, ϵ', and ϵ'', introduced in the orientation of domain walls, can take any of the two values $+1$ and -1. Sometimes it happens that the same couple of permissible planes separates two different sets (S_p, S_q) or (S_r, S_s) of OS. We shall call this couple of permissible planes doubly degenerate $(x2)$. In some species certain couples of domain walls are triply degenerate $(x3)$. The notations (S) and (P) which sometimes accompany the ferroelastic system has the same meaning as in Refs. 4 and 12: when the prototype belongs to a noncubic system, P means that the crystallographic unique axis (or an important axis) of the ferroelastic phase is along the crystallographic unique axis of the prototype and S means that these axes are orthogonal. When the prototype belongs to the cubic system, P means that the unique axis (or an important axis) of the ferroelastic phase is along one of the cubic principal axes of the prototype and S means that the unique axis (or an important axis) of the ferroelastic phase is along a face diagonal of the cubic lattice.

In Table VI we present a list of full ferroelastics; some of them are simultaneously ferroelectrics.[4,6] Consider, for instance, the case of boracities[13,14] ($Mg_3B_7O_{13}Cl$, $Fe_3B_7O_{13}Cl$) of species $\bar{4}3mFmm2$. There are six OS, all different in spontaneous polarization vectors $\vec{P}_s$ as well as in spontaneous strain. $\vec{P}_s$ is directed along the [100], [010], and [001] axes of the prototypic phase. The orientations of permissible domain walls are given in Table II, part 1. At null stress the six domain types can coexist in the same sample. In case $\vec{P}_s$ vectors would be antiparallel in the two domains under consideration, the boundary between the domains can be one of the planes parallel to the cube faces and containing $\vec{P}_s$; whenever $\vec{P}_s$ vectors make a 90° angle, the domains are separated either by a bisector plane of the cube or by a W' wall perpendicular to this plane, the orientation of which depends on the relative value of the nonzero components b and d of the spontaneous strain tensor. The species of KCN and NaCN ($m3mFmmm$) corresponds[15,16] to pure ferroelastics; but the domain-wall orientations predicted are exactly the same as in boracites. There are 21 crystallographically different directions of permissible planes. The domains being numerous and of small dimensions in KCN and NaCN, the crystals seem to be rather opaque below T_c, but recover their transparency when returning to the cubic phase.

Sb_5O_7I and $BiVO_4$ are new ferroelastics which belong, respectively,[17,18] to $6/mF2/m$ and $4/mF2/m$. These species are such that between two domains the permissible walls predicted are two perpendicular W' planes.

Recently it has been found that crystals of composition $Nd_xLa_{1-x}P_5O_{14}$ $(0 \leq x \leq 1)$ are pure ferroelastics.[19] The two permissible domain-wall orientations predicted (Table IV, part 12) have been observed. These planes do not differ in orientations from domain walls in Rochelle salt[20] ($222F2$), which is simultaneously ferroelectric ($\vec{P}_s$ parallel to the monoclinic 2 axis).

IV. SITUATION WHEN NO PERMISSIBLE DOMAIN WALLS ARE PREDICTED

We have already seen (Sec. I) that the existence of a physical solution of Eq. (3) is subject to condition (4). If Eq. (4) is not satisfied, no permissible walls between the considered S and S' domains are then predicted by our theory. The paragraphs relative to species where such a situation occurs are indicated in Tables I–V by an asterisk. The question which naturally arises is, what would be the boundaries between S and S' in crystals belonging to those species? The answer is that in principle these domains cannot be adjacent in the same crystal. Nevertheless, if S and S' coexist in the same crystal, they are then separated by intermediate OS such that condition (4) remains verified between adjacent domains. Yet, two domains between which no permissible walls are predicted can be observed adjoining in the same crystal, generally when applying an external stress. The boundaries are then often irregular, curved, or diffuse walls, connected with large internal stresses and energies. In ferroelastics, which are simultaneously ferroelectrics, permissible domain walls are more easily movable in an external electric field than these last boundaries, which actually involve important mismatch of the crystalline structure.

Let us consider, for example, the case[21] of $CH_3NH_3Al(SO_4)_2 \cdot 12H_2O$ (MASD) which belongs to

TABLE IV. Domain-wall orientations in ferroelastics, monoclinic system.

1. * Cubic 1 → Monoclinic (P) (12 ; 45)
$432F2$, $\bar{4}3mF2$, $\underline{m3mF2/m}$

$\begin{pmatrix} a & 0 & 0 \\ & b & d \\ & & c \end{pmatrix}$ monoclinic axis parallel to x, $a + b + c = 0$

x = 0	y = 0	x2
y = 0	z = 0	x2
z = 0	x = 0	x2
x = y	x = -y	x2
y = z	y = -z	x2
z = x	z = -x	x2
x = y	(a-b)(x+y) + 2dz = 0	
x = y	(a-b)(x+y) - 2dz = 0	
x = -y	(a-b)(x-y) + 2dz = 0	
x = -y	(a-b)(x-y) - 2dz = 0	
x = y	(c-a)(x+y) + 2dz = 0	
x = y	(c-a)(x+y) - 2dz = 0	
x = -y	(c-a)(x-y) + 2dz = 0	
x = -y	(c-a)(x-y) - 2dz = 0	
y = z	(a-b)(y+z) + 2dx = 0	
y = z	(a-b)(y+z) - 2dx = 0	
y = -z	(a-b)(y-z) + 2dx = 0	
y = -z	(a-b)(y-z) - 2dx = 0	
y = z	(c-a)(y+z) + 2dx = 0	
y = z	(c-a)(y+z) - 2dx = 0	
y = -z	(c-a)(y-z) + 2dx = 0	
y = -z	(c-a)(y-z) - 2dx = 0	
z = x	(a-b)(z+x) + 2dy = 0	
z = x	(a-b)(z+x) - 2dy = 0	
z = -x	(a-b)(z-x) + 2dy = 0	
z = -x	(a-b)(z-x) - 2dy = 0	
z = x	(c-a)(z+x) + 2dy = 0	
z = x	(c-a)(z+x) - 2dy = 0	
z = -x	(c-a)(z-x) + 2dy = 0	
z = -x	(c-a)(z-x) - 2dy = 0	
x = ny	x = - y/n	
x = - ny	x = y/n	
y = nz	y = - z/n	
y = - nz	z = z/n	
z = nx	z = - x/n	
z = - nx	z = x/n	

with $n = \left\{2d + \left(4d^2 + (c-b)^2\right)^{1/2}\right\} / (c-b)$

2. * Cubic 1 → Monoclinic (S) (12 ; 45)
$432F2$, $\bar{4}3mFm$, $\underline{m3mF2/m}$

$\begin{pmatrix} -2b & e & e \\ & b & d \\ & & b \end{pmatrix}$ monoclinic axis parallel to $[00\bar{1}]$

x = 0	y = z
x = 0	y = -z
x = 0	ey + dz = 0
x = 0	-ey + dz = 0
x = 0	ez + dy = 0
x = 0	-ez + dy = 0
y = 0	z = x
y = 0	z = -x
y = 0	ez + dx = 0
y = 0	-ez + dx = 0
y = 0	ex + dz = 0
y = 0	-ex + dz = 0
z = 0	x = y
z = 0	x = -y
z = 0	ex + dy = 0
z = 0	-ex + dy = 0
z = 0	ey + dx = 0
z = 0	-ey + dx = 0
x = y	-3b(x+y) + 2z(d+e) = 0
x = y	-3b(x+y) - 2z(d+e) = 0
x = y	-3b(x+y) + 2z(d-e) = 0
x = y	-3b(x+y) - 2z(d-e) = 0
x = -y	-3b(x-y) + 2z(d+e) = 0
x = -y	-3b(x-y) - 2z(d+e) = 0
x = -y	-3b(x-y) + 2z(d-e) = 0
x = -y	-3b(x-y) - 2z(d-e) = 0
y = z	-3b(y+z) + 2x(d+e) = 0
y = z	-3b(y+z) - 2x(d+e) = 0
y = z	-3b(y+z) + 2x(d-e) = 0
y = z	-3b(y+z) - 2x(d-e) = 0
y = -z	-3b(y-z) + 2x(d+e) = 0
y = -z	-3b(y-z) - 2x(d+e) = 0
y = -z	-3b(y-z) + 2x(d-e) = 0
y = -z	-3b(y-z) - 2x(d-e) = 0
z = x	-3b(z+x) + 2y(d+e) = 0
z = x	-3b(z+x) - 2y(d+e) = 0
z = x	-3b(z+x) + 2y(d-e) = 0
z = x	-3b(z+x) - 2y(d-e) = 0
z = -x	-3b(z-x) + 2y(d+e) = 0
z = -x	-3b(z-x) - 2y(d+e) = 0
z = -x	-3b(z-x) + 2y(d-e) = 0
z = -x	-3b(z-x) - 2y(d-e) = 0

3. * Cubic 2 · Monoclinic (6 ; 3)
$23F2$, $\underline{m3F2/m}$

$\begin{pmatrix} a & 0 & 0 \\ & b & d \\ & & c \end{pmatrix}$ monoclinic axis parallel to x, $a + b + c = 0$

x = 0	y = 0
y = 0	z = 0
z = 0	x = 0

4. Tetragonal 1 · Monoclinic (P) (4 ; 8)
$422F2$, $4mmF2$, $\bar{4}2mF2$, $\underline{4/mmmF2/m}$

$\begin{pmatrix} -a & b & 0 \\ & a & 0 \\ & & 0 \end{pmatrix}$ monoclinic axis parallel to x

x = 0	y = 0	x2
x = y	x = -y	x2
x = py	x = -y/p	
x = -py	x = y/p	

with $p = \left[b + (b^2 + a^2)^{1/2}\right] / a$

5. Tetragonal 1 · Monoclinic (S) (4 ; 9)
$422F2$, $4mmFm$, $\bar{4}2mF2$, $\bar{4}2mFm$, $\underline{4/mmmF2/m}$

$\begin{pmatrix} -a & 0 & b \\ & a & 0 \\ & & 0 \end{pmatrix}$ monoclinic axis parallel to y

x = 0	z = 0
y = 0	z = 0
x = y	a(x+y) + bz = 0
x = y	a(x+y) - bz = 0
x = -y	a(x-y) + bz = 0
x = -y	a(x-y) - bz = 0

6. Tetragonal 1 → Monoclinic (S) (4 ; 9)
$422F2$, $4mmFm$, $\bar{4}2mF2$, $\bar{4}2mFm$, $\underline{4/mmmF2/m}$

$\begin{pmatrix} 0 & a & c \\ & 0 & c \\ & & 0 \end{pmatrix}$ monoclinic axis making 45° with x

z = 0	x = y
z = 0	x = -y
x = 0	ay + cz = 0
x = 0	ay - cz = 0
y = 0	ax + cz = 0
y = 0	ax - cz = 0

TABLE IV. (*Continued*)

7. Tetragonal 2 → Monoclinic (2 ; 2)
4F2 , $\bar{4}$F2 , 4/mF2/m

$$\begin{pmatrix} -a & b & 0 \\ & a & 0 \\ & & 0 \end{pmatrix}$$

$x = py$	$x = -y/p$

with $p = \left(b + (a^2 + b^2)^{1/2}\right)/a$

8. Hexagonal 1 → Monoclinic (P) (6 ; 18)
622F2 , 6mmF2 , $\bar{6}$m2Fm , 6/mmmF2/m

$$\begin{pmatrix} -a & b & 0 \\ & a & 0 \\ & & 0 \end{pmatrix}$$

$x = 0$	$y = 0$	x3
$x = \sqrt{3}\,y$	$x = -y/\sqrt{3}$	x3
$x = -\sqrt{3}\,y$	$x = y/\sqrt{3}$	x3
$x = qy$	$x = -y/q$	
$x = -qy$	$x = y/q$	
$x = ry$	$x = -y/r$	
$x = -ry$	$x = y/r$	
$x = sy$	$x = -y/s$	
$x = -sy$	$x = y/s$	

$q = \left(-a + (a^2 + b^2)^{1/2}\right)/b$

$r = \{3b + \sqrt{3}\,a + 2[3(a^2+b^2)]^{1/2}\}/(3a-\sqrt{3}\,b)$

$s = \{3b - \sqrt{3}\,a + 2[3(a^2+b^2)]^{1/2}\}/(\sqrt{3}\,b+3a)$

9. Hexagonal 2 → Monoclinic (3 ; 6)
6F2 , $\bar{6}$Fm , 6/mF2/m

$$\begin{pmatrix} -a & b & 0 \\ & a & 0 \\ & & 0 \end{pmatrix}$$

$x = qy$	$x = -y/q$
$x = ry$	$x = -y/r$
$x = sy$	$x = -y/s$

10. Hexagonal 1 → Monoclinic (S) (6 ; 19)
622F2 , 6mmFm , $\bar{6}$m2F2 , $\bar{6}$m2Fm , 6/mmmF2/m

$$\begin{pmatrix} -a & 0 & c \\ & a & 0 \\ & & 0 \end{pmatrix}$$ monoclinic axis parallel to y

$z = 0$	$x = 0$
$z = 0$	$x = \sqrt{3}\,y$
$z = 0$	$x = -\sqrt{3}\,y$
$x = 0$	$y = cz/a\sqrt{3}$
$x = 0$	$y = -cz/a\sqrt{3}$
$y = 0$	$z = ax/c$
$y = 0$	$z = -ax/c$
$x = \sqrt{3}\,y$	$a(3x + \sqrt{3}\,y) + 2cz = 0$
$x = \sqrt{3}\,y$	$a(3x + \sqrt{3}\,y) - 2cz = 0$
$x = -\sqrt{3}\,y$	$a(3x - \sqrt{3}\,y) + 2cz = 0$
$x = -\sqrt{3}\,y$	$a(3x - \sqrt{3}\,y) - 2cz = 0$
$x = y/\sqrt{3}$	$a(x + \sqrt{3}\,y) + 2cz = 0$
$x = y/\sqrt{3}$	$a(x + \sqrt{3}\,y) - 2cz = 0$
$x = -y/\sqrt{3}$	$a(x - \sqrt{3}\,y) + 2cz = 0$
$x = -y/\sqrt{3}$	$a(x - \sqrt{3}\,y) - 2cz = 0$

11. Trigonal 1 → Monoclinic (3 ; 6)
32F2 , 3mFm , $\bar{3}$mF2/m

$$\begin{pmatrix} -a & 0 & c \\ & a & 0 \\ & & 0 \end{pmatrix}$$ monoclinic axis parallel to y

$y = 0$	$z = -ax/c$
$y = \sqrt{3}\,x$	$a(\sqrt{3}\,y + x) - 2cz = 0$
$y = -\sqrt{3}\,x$	$a(\sqrt{3}\,y - x) + 2cz = 0$

12. Orthorhombic → Monoclinic (2 ; 2)
222F2 , mm2F2 , mm2Fm , mmmF2/m

$$\begin{pmatrix} 0 & 0 & b \\ & 0 & 0 \\ & & 0 \end{pmatrix}$$ monoclinic axis parallel to y

$x = 0$	$z = 0$

species 23*F*2; two domains with antiparallel P_s vectors directed along one of the cubic axes of the prototype are separated by any of the two permissible planes parallel to the cube faces and containing $\vec{P}_s$. The OS which are deduced one from the other by a rotation around one of the four equivalent axes [111] have their $\vec{P}_s$ vectors at 90°. No permissible walls are predicted; to make these OS adjoin, one must apply an external stress. The boundaries are then not well-defined planes which cannot be moved with electric fields smaller than the breakdown field. On the contrary, permissible domain walls are easily movable and their contribution to the process of polarization reversal is evidenced by hysteresis loops.[21] Likewise in dicadmium diammonium sulfate[21,22] (CAS) of species 23*F*2, six domains can exist but only antiparallel domains are separated by permissible walls, 90° walls being stressed. The behavior of the different walls is therefore similar to that observed in MASD.

In our systematical investigation of domain-wall orientations, we noted four species (23*F*222, *m*3*Fmmm*, 3*F*1, and $\bar{3}$*F*1) characterized by the complete lack of permissible planes. Dicadmium dithallium sulfate[23] (CTS) in its γ phase ($T < -175$ °C) belongs to the pure ferroelastic 23*F*222 species. Samples are generally single domain and contain at most two domains (probably when the crystal is cemented to the cryostat external stresses appear) among the three different expected OS. These adjacent domains are separated by boundaries not predicted by the theory. The fact that samples often crack along domain walls in the vicinity of the phase transition is an evidence of the stressed character of these boundaries.

V. PROPERTIES OF *W* AND *W*′ WALLS

We have seen before that if two ferroelastic domains S_1 and S_2 are separated by a *W* wall, their spontaneous strain tensors can be deduced one from the other by symmetry with respect to *W* which is a crystallographically prominent plane. Note that this result is true for every centrosymmetrical physical property, particularly those expressed by an even tensor. In this case, the *W* wall is a mirror plane which transforms the even tensor of S_1, to the even tensor of S_2. Thus, such centrosymmetrical properties, measured in two directions taken, respectively, in S_1 and S_2 and making the same angle θ with respect to W, possess identical values [Fig. 1(a)]. The situation is different when one considers noncentrosymmetrical physical properties, particularly those associated to odd tensors. For instance in $Gd_2(MoO_4)_3$, W walls separate domains where $\vec{P}_s$ vectors are anti-

TABLE V. Domain-wall orientations in ferroelastics, triclinic system.

1. * Cubic 1 → Triclinic (24 ; 117)

$432F1$, $\bar{4}3mF1$, $\underline{m3mF\bar{1}}$

$$\begin{pmatrix} a & f & e \\ & b & d \\ & & c \end{pmatrix} \qquad a + b + c = 0$$

$x = 0$	$fy + \varepsilon ez = 0$
$x = 0$	$fz + \varepsilon ey = 0$
$x = 0$	$ey + \varepsilon dz = 0$
$x = 0$	$ez + \varepsilon dy = 0$
$x = 0$	$dy + \varepsilon fz = 0$
$x = 0$	$dz + \varepsilon fy = 0$
$y = 0$	$dz + \varepsilon fx = 0$
$y = 0$	$dx + \varepsilon fz = 0$
$y = 0$	$ez + \varepsilon dx = 0$
$y = 0$	$ex + \varepsilon dz = 0$
$y = 0$	$fz + \varepsilon ex = 0$
$y = 0$	$fx + \varepsilon ez = 0$
$z = 0$	$fx + \varepsilon ey = 0$
$z = 0$	$fy + \varepsilon ex = 0$
$z = 0$	$ex + \varepsilon dy = 0$
$z = 0$	$ey + \varepsilon dx = 0$
$z = 0$	$dx + \varepsilon fy = 0$
$z = 0$	$dy + \varepsilon fx = 0$
$x = \varepsilon y$	$(a-b)(x+\varepsilon y) + \varepsilon'(e+\varepsilon'' d) z = 0$
$x = \varepsilon y$	$(b-c)(x+\varepsilon y) + \varepsilon'(e+\varepsilon'' f) z = 0$
$x = \varepsilon y$	$(a-c)(x+\varepsilon y) + \varepsilon'(d+\varepsilon'' f) z = 0$
$y = \varepsilon z$	$(a-b)(y+\varepsilon z) + \varepsilon'(e+\varepsilon'' d) x = 0$
$y = \varepsilon z$	$(b-c)(y+\varepsilon z) + \varepsilon'(e+\varepsilon'' f) x = 0$
$y = \varepsilon z$	$(a-c)(y+\varepsilon z) + \varepsilon'(d+\varepsilon'' f) x = 0$
$z = \varepsilon x$	$(a-b)(z+\varepsilon x) + \varepsilon'(e+\varepsilon'' d) y = 0$
$z = \varepsilon x$	$(b-c)(z+\varepsilon x) + \varepsilon'(e+\varepsilon'' f) y = 0$
$z = \varepsilon x$	$(a-c)(z+\varepsilon x) + \varepsilon'(d+\varepsilon'' f) y = 0$

2. * Cubic 2 → Triclinic (12 ; 21)

$23F1$, $\underline{m3F\bar{1}}$

$$\begin{pmatrix} a & f & e \\ & b & d \\ & & c \end{pmatrix} \qquad a + b + c = 0$$

$x = 0$	$fy + \varepsilon ez = 0$
$x = 0$	$ey + \varepsilon dz = 0$
$x = 0$	$dy + \varepsilon fz = 0$
$y = 0$	$dz + \varepsilon fx = 0$
$y = 0$	$ez + \varepsilon dx = 0$
$y = 0$	$fz + \varepsilon ex = 0$
$z = 0$	$fx + \varepsilon ey = 0$
$z = 0$	$ex + \varepsilon dy = 0$
$z = 0$	$dx + \varepsilon fy = 0$

3. * Hexagonal 1 → Triclinic (12 ; 49)

$622F1$, $6mmF1$, $\bar{6}m2F1$, $\underline{6/mmmF\bar{1}}$

$$\begin{pmatrix} -a & b & c \\ & a & d \\ & & 0 \end{pmatrix}$$

$x = 0$	$by + \varepsilon cz = 0$
$y = 0$	$bx + \varepsilon dz = 0$
$z = 0$	$cx + \varepsilon dy = 0$
$x = \varepsilon\sqrt{3}y$	$b(y+\varepsilon\sqrt{3}x) + 2\varepsilon' cz = 0$
$y = \varepsilon\sqrt{3}x$	$b(x+\varepsilon\sqrt{3}y) + 2\varepsilon' dz = 0$
$x = 0$	$(\varepsilon\sqrt{3}a+b)y + \varepsilon'(c-\varepsilon\sqrt{3}d)z = 0$
$y = 0$	$(\varepsilon\sqrt{3}a+b)x + \varepsilon'(\sqrt{3}c+\varepsilon d)z = 0$
$z = 0$	$(c+\varepsilon\sqrt{3}d)x + \varepsilon'(d-\varepsilon\sqrt{3}c)y = 0$
$x = \varepsilon\sqrt{3}y$	$(b+\varepsilon' a\sqrt{3})(y+\varepsilon\sqrt{3}x)+2z\varepsilon''(d\sqrt{3}-\varepsilon' c) = 0$
$y = \varepsilon\sqrt{3}x$	$(b+\varepsilon' a\sqrt{3})(x+\varepsilon\sqrt{3}y)+2z\varepsilon''(c\sqrt{3}+\varepsilon' d) = 0$

4. * Hexagonal 2 → Triclinic (6 ; 4)

$6F1$, $\bar{6}F1$, $\underline{6/mF\bar{1}}$

$$\begin{pmatrix} -a & b & c \\ & a & d \\ & & 0 \end{pmatrix}$$

$z = 0$	$cx + dy = 0$
$z = 0$	$x(c-\sqrt{3}\,d) + y(\sqrt{3}\,c+d) = 0$
$z = 0$	$x(c+\sqrt{3}\,d) - y(\sqrt{3}\,c-d) = 0$

TABLE V. (*Continued*)

5. * Trigonal 1 → Triclinic (6 ; 12)
32F1 , 3mF1 , $\bar{3}mF\bar{1}$

$$\begin{pmatrix} -a & b & c \\ & a & d \\ & & 0 \end{pmatrix}$$

$x = 0$	$by + cz = 0$
$x = 0$	$(\sqrt{3}\,a + b)\,y + (c - \sqrt{3}\,d)\,z = 0$
$x = 0$	$(\sqrt{3}\,a - b)\,y - (c + \sqrt{3}\,d)\,z = 0$
$x = \sqrt{3}y$	$b(y + \sqrt{3}\,x) - 2cz = 0$
$x = \sqrt{3}y$	$(\sqrt{3}a+b)(y+\sqrt{3}x)-2z(c-\sqrt{3}d) = 0$
$x = \sqrt{3}y$	$(\sqrt{3}a-b)(y+\sqrt{3}x)+2z(c+\sqrt{3}d) = 0$
$x = -\sqrt{3}y$	$b(y - \sqrt{3}\,x) - 2cz = 0$
$x = -\sqrt{3}y$	$(\sqrt{3}a+b)(y-\sqrt{3}x)-2z(c-\sqrt{3}d) = 0$
$x = -\sqrt{3}y$	$(\sqrt{3}a-b)(y-\sqrt{3}x)+2z(c+\sqrt{3}d) = 0$

6. * Trigonal 2 → Triclinic (3 ; 0)
3F1 , $\bar{3}F\bar{1}$

$$\begin{pmatrix} -a & b & c \\ & a & d \\ & & 0 \end{pmatrix}$$

No permissible domain walls

7. * Tetragonal 1 → Triclinic (8 ; 25)
422F1 , 4mmF1 , $\bar{4}2mF1$, $4/mmmF\bar{1}$

$$\begin{pmatrix} -a & b & c \\ & a & d \\ & & 0 \end{pmatrix}$$

$x = 0$	$\varepsilon by + cz = 0$
$x = 0$	$\varepsilon by + dz = 0$
$y = 0$	$\varepsilon bx + cz = 0$
$y = 0$	$\varepsilon bx + dz = 0$
$z = 0$	$\varepsilon cx + dy = 0$
$z = 0$	$\varepsilon dx + cy = 0$
$y = \varepsilon x$	$a(y+\varepsilon x) + \varepsilon'(d+\varepsilon''c)z = 0$

8. * Tetragonal 2 → Triclinic (4 ; 3)
4F1 , $\bar{4}F1$, $4/mF\bar{1}$

$$\begin{pmatrix} -a & b & c \\ & a & d \\ & & 0 \end{pmatrix}$$

$z = 0$	$cx + dy = 0$
$z = 0$	$-dx + cy = 0$

9. Orthorhombic → Triclinic (4 ; 9)
222F1 , mm2F1 , $mmmF\bar{1}$

$$\begin{pmatrix} 0 & c & b \\ & 0 & a \\ & & 0 \end{pmatrix}$$

$x = 0$	$bz + cy = 0$
$x = 0$	$bz - cy = 0$
$y = 0$	$az + cx = 0$
$y = 0$	$az - cx = 0$
$z = 0$	$ay + bx = 0$
$z = 0$	$ay - bx = 0$

10. Monoclinic → Triclinic (2 ; 2)
2F1 , mF1 , $2/mF\bar{1}$

$$\begin{pmatrix} 0 & a & 0 \\ & 0 & b \\ & & 0 \end{pmatrix}$$

$y = 0$	$ax + bz = 0$

parallel.

Consider now an acoustic plane wave impinging on a W wall. The acoustical velocity depends on the direction of propagation, but evidently not on the orientation of the propagation vector $\vec{K}$. Therefore, it is a centrosymmetrical physical property and to two directions symmetrical with respect to W, corresponds in the two adjoining domains, the same value for the velocity. Snell's laws[24] indicate then that reflection and refraction occur at equal angles with respect to W. Generally an incident wave gives rise to three reflected and three refracted waves represented in Fig. 1(b). The experimental evidence of the laws of reflection and refraction on W walls has been given in the case of $Gd_2(MoO_4)_3$ using acousto-optical methods.[25] Likewise it is evident that reflection and refraction of plane light waves also occurs at symmetrical angles with respect to W. Yet there are in this case only two reflected and two refracted waves.

It is well known that spontaneous strain varies

TABLE VI. List of ferroelastic crystals belonging to different species. Domain structures have been observed in all the listed materials. W walls are generally the first to be identified in crystals but the exact orientations of the observed W' walls have not yet been determined experimentally except in the case of $Pb_3(PO_4)_2$.

Materials	Species	T_c (°C)	Corresponding table and part	Ferroelectric
$SrTiO_3$[a]	$m3mF4/mmm$	−163	I	
$KMnF_3$[b]	$m3mF4/mmm$	−89	I	
$CsPbCl_3$[c]	$m3mF4/mmm$	47	I	
V_3Si[d]	$m3mF4/mmm$	−252	I	
Nb_3Sn[d]	$m3mF4/mmm$	−230	I	
KCN[e,f]	$m3mFmmm$	−105	II 1	
NaCN[e,f]	$m3mFmmm$	15	II 1	
$Mg_3B_7O_{13}Cl$[g]	$\bar{4}3mFmm2$	265	II 1	yes
$Fe_3B_7O_{13}Cl$[h]	$\bar{4}3mFmm2$	334	II 1	yes
$Tl_2Cd_2(SO_4)_3$[i]	$23F222$	−175	II 3	
$CsPbCl_3$[c]	$4/mmmFmmm$	42	II 4	
$RbFeF_3$[j]	$4/mmmFmmm$	600	II 4	
$CsFeF_4$[j]	$4/mmmFmmm$		II 4	
KH_2PO_4 (KDP)[k]	$\bar{4}2mFmm2$	−152	II 4	yes
$Gd_2(MoO_4)_3$[l]	$\bar{4}2mFmm2$	160	II 4	yes
Tanane[m]	$\bar{4}2mFmm2$	14	II 4	yes
$NH_4H_2PO_4$ (ADP)[n]	$\bar{4}2mF222$	−125	II 5	
$LaAlO_3$[o]	$m3mF\bar{3}m$	550	III	
$PrAlO_3$[o]	$m3mF\bar{3}m$	1050	III	
$NdAlO_3$[o]	$m3mF\bar{3}m$	1370	III	
$Fe_3B_7O_{13}Cl$[p]	$\bar{4}3mF3m$	250	III	yes
$CH_3NH_3Al(SO_4)_2 \cdot 12H_2O$ (MASD)[q]	$23F2$	−96	IV 3	yes
$(NH_4)_2Cd_2(SO_4)_3$[q,r]	$23F2$	−178	IV 3	yes
$Tl_2Cd_2(SO_4)_3$[i]	$23F2$	−146	IV 3	yes
VO_2[s]	$4/mmmF2/m$	70	IV 5	
$BiVo_4$[t]	$4/mF2/m$	255	IV 7	
Sb_5O_7I[u]	$6/mF2/m$	208	IV 9	
$(PO_4)_2Pb_3$[v,w]	$\bar{3}mF2/m$	185	IV 11	
NaN_3[x]	$\bar{3}mF2/m$	20	IV 11	
$NaKC_4H_4O_6 \cdot 4H_2O$[y] (Rochelle salt)	$222F2$	−18, +24	IV 12	yes
NdP_5O_{14}[z]	$mmmF2/m$	145	IV 12	
$Nd_{0.75}La_{0.25}P_5O_{14}$[z]	$mmmF2/m$	141	IV 12	
$Tl_2Cd_2(SO_4)_3$[i]	$23F1$	−143	V 2	yes

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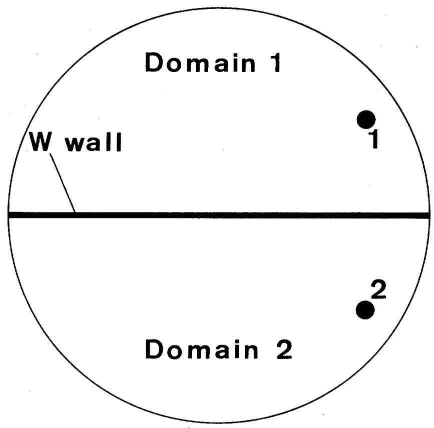
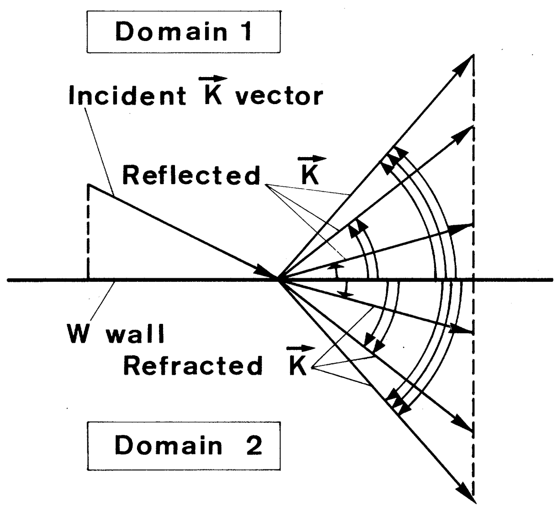


(a)



(b)

FIG. 1. (a) Stereographic projection of a ferroelastic crystal; the origin of the stereogram is chosen on a W plane (represented vertical). Every centrosymmetrical physical property takes identical values in two directions symmetrical with respect to W (each direction is represented by a black dot in the domain under consideration). (b) Reflection and refraction of an acoustic incident wave on the surface of a W wall in a ferroelastic. All the waves are represented by their $\vec{K}$ vector. The incident and the scattered waves must all have the same components of $\vec{K}$ parallel to the boundary. This condition is the basis of deriving Snell's laws. The symmetries of the physical properties represented by the slowness curve then lead to the equality of the angles of reflection and refraction (Ref. 25).

with temperature and vanishes above T_c. The form of the tensor remains the same but the different components change their values. Besides, we have established that W' planes have orientations, which depend on the relative values of the nonzero components of this tensor. In the case of $Pb_3(PO_4)_2$ given in Sec. II, we established that the angle θ between the W' wall and the z axis is equal to $(\arctan c/a)$. The a component decreases[11] by a factor of four to five from room temperature to the critical temperature (~180 °C) when $Pb_3(PO_4)_2$ undergoes a first-order transition.[26] Yet nothing was known about c variation till now. We have since observed a slight angular variation of θ versus temperature and this leads to the conclusion that the ratio c/a does not remain constant. More details on this experiment will be published elsewhere.

Before we conclude let us make an important remark. Actually the orientations of permissible domain walls reported in Tables I, II, III, IV, and V are given in the prototypic phase (or, for a crystal undergoing a second-order transition, in the ferroelastic phase just at the critical point T_c). It is then easy to understand that in the ferroelastic phase the angle between the two permissible orientations between two given domains is submitted to a slight modification owing precisely to the spontaneous strain. This angle varies about 90° versus temperature in the same manner as the spontaneous strain. Consider, for instance, the case of $Gd_2(MoO_4)_3$: the two possible orientations of the walls ($x=0$, $y=0$) make an angle which differs from 90° by an amount of 10′, which is precisely equal to twice the value of the shear component[27,28] at $T=20$ °C. Generally speaking, the angle between the orientations of the two walls which separate an i-type domain from other j-type domains, thus provides the value of the components of the spontaneous strain, or, at least a relation between these components.

VI. CONCLUSION

Physical studies of ferroelasticity as well as the number of new ferroelastic compounds have increased in the last few years. The first sign of ferroelasticity is generally revealed in a crystal by the appearance of domain structures which can be easily observed under a polarizing microscope most ferroelastics being transparent in the visible spectrum. Indeed, two OS differing in spontaneous strain also differ in refractive indices. The presence of ferroelasticity is generally confirmed by modification of the domain structures when applying an appropriate mechanical stress. On the contrary, in pure ferroelectrics like $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (TGS) and $LiNbO_3$, two different OS are not different in refractive-index tensor and the procedure of observation of domain structures is much more complicated (by surface etching, by deposit of electrostatically charged powders, etc.).

Starting from the same basic assumption as in

Ref. 2 (i.e.: the change in length, due to spontaneous strain, of any infinitesimal vector contained in a wall, is equal in the two adjacent domains), we have determined the allowed domain-wall orientations in all ferroelastic species. The procedure we used has the advantage of not introducing physical properties such as spontaneous polarization, piezoelectricity, or electrostriction, but depends only on the well-known form of the spontaneous strain tensor as expressed in Ref. 4. The symmetries of this tensor are related to the holohedry or the hemihedry of the two crystallographic classes, which constitute the ferroelastic species. Moreover, the values of its components can be deduced from cell parameters of the ferroelastic phase or measured through modifications of a planar surface of a single domain crystal. These modifications arise as soon as the domain structures appear.[19,27] Another method consists of measuring the exact angle between the walls which separate two domain types, as indicated in Sec. V.

We have established that between two domains there exist two possible orientations for permissible planar walls. Prominent walls are labeled W and have an orientation crystallographically invariant with respect to temperature. In contrast to W walls, W' wall orientations are dependent on the relative values of spontaneous strain tensor components. When no permissible walls are predicted between two domains, they nevertheless can be sometimes adjacent but this situation induces an appreciable crystalline mismatch in the vicinity of the boundary.

All ferroelastic species have been explored and all possible orientations of permissible walls are given for each of them. The domain structures being characteristic of the species, Tables I–V then give the opportunity of identifying the species of a crystal by direct optical observation.

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APPENDIX

Let S^1 and S^2 be the spontaneous strain tensors of a ferroelastic material which possesses only two OS, labeled 1 and 2. S^1 and S^2 are given[4] by

$$S^1 = \sigma^1 - \tfrac{1}{2}(\sigma^1 + \sigma^2)\ , \tag{A1}$$

$$S^2 = \sigma^2 - \tfrac{1}{2}(\sigma^1 + \sigma^2) \tag{A2}$$

where σ^1 and σ^2 are strain tensors having, respectively, the symmetry elements of the point group of 1 and 2.

Adding Eqs. (A1) and (A2), one obtains

$$S^1 + S^2 = 0\ . \tag{A3}$$

Applying relation (3) to the considered OS and taking Eq. (A3) into account leads to,

$$S^1_{ij}\, x_i\, x_j = 0 \quad \text{or} \quad S^2_{ij}\, x_i\, x_j = 0$$

in the fixed orthogonal system of the prototypic phase. Thus permissible walls between 1 and 2 are in this case planes containing the directions of the prototype for which no change in length occurs in the two OS. This result is valid whatever the nature of the walls (W or W'), but cannot be generalized to ferroelastics including more than two OS.

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